Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)

2. REPORT DATE 3/26/08

3. REPORT TYPE AND DATES COVERED
Final Technical Report 15/5/06 - 14/11/07

4. TITLE AND SUBTITLE
New Synthesis for Lanthanum Hexaboride Nanocrystals

5. FUNDING NUMBERS
W911NF-06-1-0176

6. AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Yale University
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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U. S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
50907.1-MS

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
NA

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	**UNCLASSIFIED**	**UNCLASSIFIED**	**UU**

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. 239-18
298-102

Enclosure 1

Final report
Army Office of Research W911NF-06-1-0176

New Synthesis for Lanthanum Hexaboride Nanocrystals

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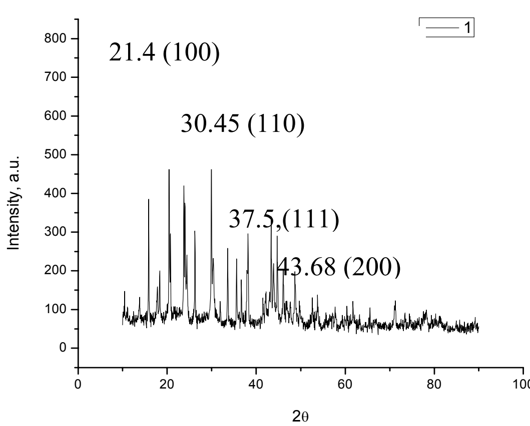
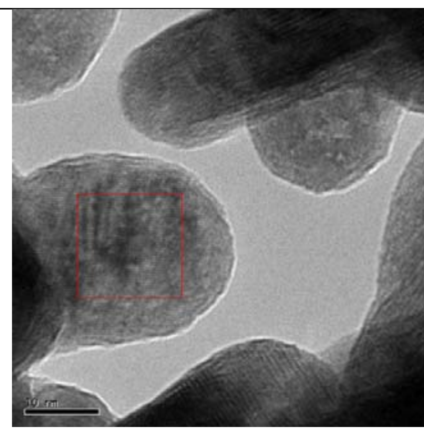
Although lanthanum hexaboride has been used for many years as a cathode material, new applications exploiting its unusual electron emission properties are now being investigated [Boustani *et al*., Monnier and Delley]. Nanocrystalline LaB_6 materials have been predicted to provide important advantages for IR absorbers as well as for nanoelectronics in general because of their low work function. Lanthanum hexaboride is usually made by mixing La and B with Al in a furnace at 1500K. The molten flux method precipitates large crystals (see *eg*. Inoue *et al*.]. This method, however, is not suitable for *nanocrystal* production.

We have synthesized LaB_6 nanocrystals for the first time using a low temperature sonochemical synthesis. Several different types of crystals were synthesized. First, 20-200nm diameter crystals were synthesized using lithium borohydride and lanthanum carbonate sonicated in a tetrahydrofuran solvent. These showed a good XRD pattern confirming the lanthanum hexaboride structure (see figure #1a and b below).

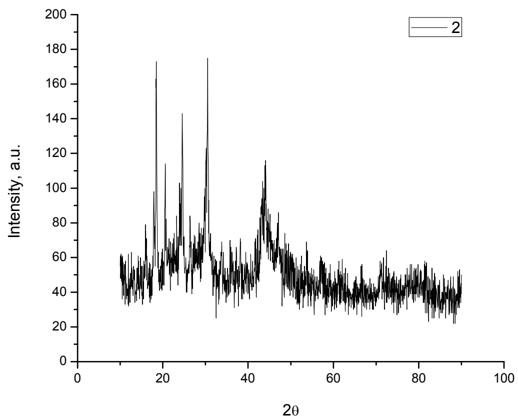


Figure#1a: XRD of LaB_6 crystals (synthesis with La carbonate)

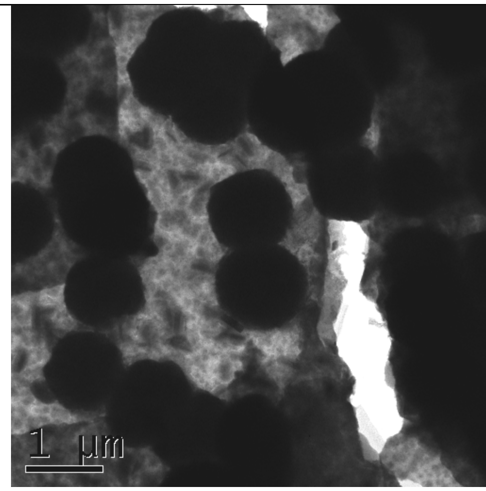


Figure#1b: TEM of LaB_6 crystals synthesized with La carbonate, scale bar is 10nm. Particle size can vary from 20-200nm depending on process conditions.

We also showed that we can control the thickness of the crystals using addition of HCl during the synthesis. A small amount of HCl acid in the synthesis leads to thinner/smaller crystalline domains and reduces the amorphous material; adding more HCl results in further thinning as observed by further significant broadening of the peaks in XRD. (see XRD Figure #2a where as acid is added the lines widen considerably).

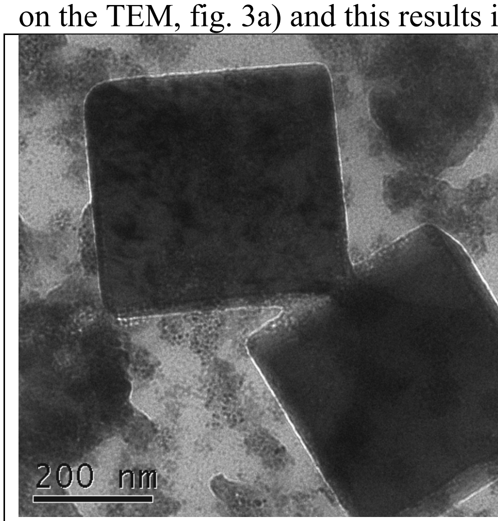


Figure#2a: XRD of LaB_6 crystals (synthesis with La carbonate with HCl addition)

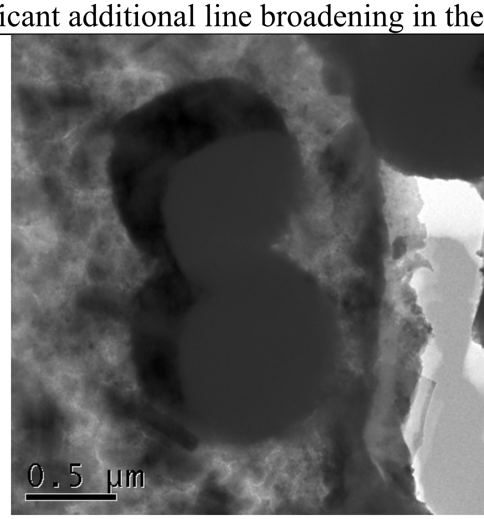


Figure#2b:TEM of LaB_6 crystals (synthesis with La carbonate with HCl addition)

The crystals in one run adding additional HCl were very thin (you can see through them on the TEM, fig. 3a) and this results in significant additional line broadening in the XRD.



Figure#3a: TEM of LaB_6 crystals (synthesis with La carbonate with further HCl addition after cleaning step)



Figure#3b:TEM (Closer view) of LaB_6 crystals (synthesis with La carbonate with HCl addition) shown in figure 2b.

A different synthesis strategy using Lanthanum chloride as the La precursor resulted in smaller (several nm diameter) boron/lanthanum/oxygen particles which could likely be annealed at high T to give LaB_6. Another strategy using the same precursor with water as the solvent resulted in a purple powder containing amorphous boron/lanthanum particles 3-5 nm in diameter which will likely be able to be converted to LaB_6 on annealing at high temperature. An oven is currently being installed that will allow us to anneal samples in varied environments up to 1900K.

Thus several different routes to varied structure LaB_6 nanocrystals have been demonstrated. This is extremely promising because it means that the LaB_6 crystals can be designed by varying the synthesis strategy to meet varied application needs. Initial work suggests that reasonably narrow diameter distributions of crystals with mean diameters ranging from 5-200nm can likely be synthesized and that the aspect ratio can be varied and surface orientation can likely be varied. Issues that need to be addressed in future research are parameter optimization to control particle structure and purity issues.

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